

A HYDROGEN STORAGE MATERIAL INCLUDING A MODIFIED TI-MN₂ ALLOY

FIELD OF THE INVENTION

The instant invention relates generally to hydrogen storage materials and more specifically to hydrogen storage materials including a modified TiMn₂ alloy. The hydrogen storage materials also include a support means such as a metal mesh, grid, matte, foil, foam or plate.

BACKGROUND OF THE INVENTION

In the past considerable attention has been given to the use of hydrogen as a fuel or fuel supplement. While the world's oil reserves are rapidly being depleted, the supply of hydrogen remains virtually unlimited. Hydrogen can be produced from coal, natural gas and other hydrocarbons, or formed by the electrolysis of water. Moreover hydrogen can be produced without the use of fossil fuels, such as by the electrolysis of water using nuclear or solar energy. Furthermore, hydrogen, although presently more expensive than petroleum, is a relatively low cost fuel. Hydrogen has the highest density of energy per unit weight of any chemical fuel and is essentially non-polluting since the main by-product of burning hydrogen is water.

While hydrogen has wide potential application as a fuel, a major drawback in its utilization, especially in mobile uses such as the powering of vehicles, has been the lack of acceptable lightweight hydrogen storage medium. Conventionally, hydrogen has been stored in a pressure-resistant vessel under a high pressure or stored as a cryogenic liquid, being cooled to an extremely low temperature. Storage of hydrogen as a compressed gas

involves the use of large and heavy vessels. In a steel vessel or tank of common design only about 1% of the total weight is comprised of hydrogen gas when it is stored in the tank at a typical pressure of 136 atmospheres. In order to obtain equivalent amounts of energy, a container of hydrogen gas weighs about thirty times the weight of a container of gasoline. Additionally, transfer is very difficult, since the hydrogen is stored in a large-sized vessel; amount of hydrogen stored in a vessel is limited, due to low density of hydrogen. Furthermore, storage as a liquid presents a serious safety problem when used as a fuel for motor vehicles since hydrogen is extremely flammable. Liquid hydrogen also must be kept extremely cold, below -253.degree. C., and is highly volatile if spilled. Moreover, liquid hydrogen is expensive to produce and the energy necessary for the liquefaction process is a major fraction of the energy that can be generated by burning the hydrogen.

Alternatively, certain metals and alloys have been known to permit reversible storage and release of hydrogen. In this regard, they have been considered as a superior hydrogen-storage material, due to their high hydrogen-storage efficiency. Storage of hydrogen as a solid hydride can provide a greater volumetric storage density than storage as a compressed gas or a liquid in pressure tanks. Also, hydrogen storage in a solid hydride presents fewer safety problems than those caused by hydrogen stored in containers as a gas or a liquid. Solid-phase metal or alloy system can store large amounts of hydrogen by absorbing hydrogen with a high density and by forming a metal hydride under a specific temperature/pressure or electrochemical conditions, and hydrogen can be released by changing these conditions. Metal hydride systems have the advantage of high-density hydrogen-storage for long periods of time, since they are formed by the insertion of hydrogen atoms to the crystal lattice of a metal. A desirable hydrogen storage

material must have a high storage capacity relative to the weight of the material, a suitable desorption temperature/pressure, good kinetics, good reversibility, resistance to poisoning by contaminants including those present in the hydrogen gas and be of a relatively low cost. If the material fails to possess any one of these characteristics it will not be acceptable for wide scale commercial utilization.

The hydrogen storage capacity per unit weight of material is an important consideration in many applications, particularly where the hydride does not remain stationary. A low hydrogen storage capacity relative to the weight of the material reduces the mileage and hence the range of a vehicle making the use of such materials. A low desorption temperature is desirable to reduce the amount of energy required to release the hydrogen. Furthermore, a relatively low desorption temperature to release the stored hydrogen is necessary for efficient utilization of the available exhaust heat from vehicles, machinery, or other similar equipment.

Good reversibility is needed to enable the hydrogen storage material to be capable of repeated absorption-desorption cycles without significant loss of its hydrogen storage capabilities. Good kinetics are necessary to enable hydrogen to be absorbed or desorbed in a relatively short period of time. Resistance to contaminants to which the material may be subjected during manufacturing and utilization is required to prevent a degradation of acceptable performance.

The prior art hydrogen storage materials include a variety of metallic materials for hydrogen-storage, e.g., Mg, Mg-Ni, Mg-Cu, Ti-Fe, Ti-Ni, Mm-Ni and Mm-Co alloy systems (wherein, Mm is Misch metal, which is a rare-earth metal or combination/alloy of rare-earth

metals). None of these prior art materials, however, has had all of the required properties required for a storage medium with widespread commercial utilization.

Of these materials, the Mg alloy systems can store relatively large amounts of hydrogen per unit weight of the storage material. However, heat energy must be supplied to release the hydrogen stored in the alloy, because of its low hydrogen dissociation equilibrium pressure at room temperature. Moreover, release of hydrogen can be made, only at a high temperature of over 250 °C along with the consumption of large amounts of energy.

The rare-earth (Misch metal) alloys have their own problems. Although they typically can efficiently absorb and release hydrogen at room temperature, based on the fact that it has a hydrogen dissociation equilibrium pressure on the order of several atmospheres at room temperature, their hydrogen-storage capacity per unit weight is lower than any other hydrogen-storage material and they are very expensive.

The Ti-Fe alloy system which has been considered as a typical and superior material of the titanium alloy systems, has the advantages that it is relatively inexpensive and the hydrogen dissociation equilibrium pressure of hydrogen is several atmospheres at room temperature. However, since it requires a high temperature of about 350 °C and a high pressure of over 30 atmospheres for initial hydrogenation, the alloy system provides relatively low hydrogen absorption/desorption rate. Also, it has a hysteresis problem which hinders the complete release of hydrogen stored therein.

Under the circumstances, a variety of approaches have been made to solve the problems of the prior art and to develop an improved material which has a high

hydrogen-storage efficiency, a proper hydrogen dissociation equilibrium pressure and a high absorption/desorption rate.

In this regard, Ti-Mn alloy system has been reported to have a high hydrogen-storage efficiency and a proper hydrogen dissociation equilibrium pressure, since it has a high affinity for hydrogen and low atomic weight to allow large amounts of hydrogen-storage per unit weight.

Unfortunately there is still a need in the art for a low cost, high hydrogen-storage efficiency, good dissociation equilibrium pressure, high absorption/desorption, rate room temperature hydrogen storage alloy.

SUMMARY OF THE INVENTION

The instant invention is a hydrogen storage material which includes a modified Ti-Mn₂ hydrogen storage alloy. The alloy generally is comprised of Ti and Mn. A generic formula for the alloy is: Ti_{Q-X}Zr_XMn_{Z-Y}A_Y, where A is generally one or more of V, Cr, Fe, Ni and Al. Most preferably A is one or more of V, Cr, and Fe. The subscript Q is preferably between 0.9 and 1.1, and most preferably Q is 1.0. The subscript X is between 0.0 and 0.35, more preferably X is between 0.1 and 0.2, and most preferably X is between 0.1 and 0.15. The subscript Y is preferably between 0.3 and 1.8, more preferably Y is between 0.6 and 1.2, and most preferably Y is between 0.6 and 1.0. The subscript Z is preferably between 1.8 and 2.1, and most preferably Z is between 1.8 and 2.0. The alloys are generally single phase materials, exhibiting a hexagonal C₁₄ Laves phase crystalline structure.

The hydrogen storage material is comprised of the hydrogen storage alloy powder physically bonded to a support means by compaction and/or sintering. The support means is at least one of mesh, grid, matte, foil, foam or plate and is preferably formed from a metal such as one or more of Ni, Al, Cu, Fe and mixtures or alloys thereof. The hydrogen storage alloy powder which is bonded to the support means can be spirally wound into a coil or a plurality of them can be stacked as disks or plates.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1, is a Pressure-Composition-Temperature (PCT) graph for several hydrogen storage alloys of the instant invention;

Figure 2 is a PCT graph of alloy TA-34 of the instant invention;

Figure 3 is an X-ray diffraction (XRD) analysis of alloy TA-34 of the instant invention;

Figure 4 is a PCT graph of alloy TA-56 of the instant invention;

Figure 5 is a PCT graph of alloy TA-56D of the instant invention;

Figure 6 shows an embodiment of the instant invention where the support means bonded with the hydrogen storage alloy material is spirally wound into a coil; and

Figure 7 shows an alternate embodiment of the instant invention where the support means bonded with the hydrogen storage alloy material is assembled as a plurality of stacked disks.

DETAILED DESCRIPTION OF THE INVENTION

One aspect of the instant invention is a modified Ti-Mn₂ hydrogen storage alloy. The alloy generally is comprised of Ti and Mn. A generic formula for the alloy is:

$Ti_{Q-X}Zr_XMn_{Z-Y}A_Y$, where A is generally one or more of V, Cr, Fe, Ni and Al. Most preferably A is one or more of V, Cr, and Fe. The subscript Q is preferably between 0.9 and 1.1, and most preferably Q is 1.0. The subscript X is between 0.0 and 0.35, more preferably X is between 0.1 and 0.2, and most preferably X is between 0.1 and 0.15. The subscript Y is preferably between 0.3 and 1.8, more preferably Y is between 0.6 and 1.2, and most preferably Y is between 0.6 and 1.0. The subscript Z is preferably between 1.8 and 2.1, and most preferably Z is between 1.8 and 2.0. The alloys are generally single phase materials, exhibiting a hexagonal C_{14} Laves phase crystalline structure. Preferred alloys are shown in Table 1.

These alloys have average storage capacity, ranging from 1 to 2 weight percent. They also have excellent room temperature kinetics. Figure 1, is a Pressure-Composition-Temperature (PCT) graph for several of the alloys of the instant invention plotting pressure in Torr on the y-axis versus weight percent of stored hydrogen on the x-axis. Specifically shown are the desorption PCT curves for TA-1, TA-9, TA-10 and TA-11 at 30 °C. Figure 2 is a PCT graph of TA-34 at 30 °C (the ♦ symbol) and 45 °C (the ● symbol) plotting pressure in Torr on the y-axis versus weight percent of stored hydrogen on the x-axis. As can be seen, these alloys have very good plateau pressures at room temperature. The plateau pressures at 30 °C, the maximum storage capacity and the reversible storage capacity (also at 30 °C) of most of the alloys of Table 1 are shown in Table 2. It should be noted that alloys TA-34, TA-35, TA-56 and TA-56D are lower cost alloys which have reduced V and Cr content and can be made using commercially available ferrovavadium and ferrochromium alloys. Figure 3 is an X-ray diffraction (XRD) analysis of alloy TA-34.

As can be seen analysis of the XRD plot, the alloys of the instant invention have a hexagonal C₁₄ Laves phase crystalline structure.

Figure 4 is a PCT graph of TA-56 at 30 °C (adsorption is solid line, desorption is the dashed line) plotting pressure in Bar on the y-axis versus weight percent of stored hydrogen on the x-axis. Figure 5 is a PCT graph of TA-56D at 30 °C (adsorption is dashed line, desorption is the solid line) plotting pressure in Bar on the y-axis versus weight percent of stored hydrogen on the x-axis.

TABLE 1

Alloy #	Ti	Zr	V	Cr	Mn	Fe	Ni	Al
TA-1	0.9	0.1	0.45	-	1.3	-	0.26	-
TA-2	0.8	0.2	0.4	0.3	1.25	0.06	-	-
TA-4	0.8	0.2	0.4	-	1.25	0.36	-	-
TA-5	0.7	0.3	0.3	-	1.5	-	0.17	-
TA-9	0.8	0.2	0.45	-	1.3	-	0.26	-
TA-10	0.95	0.05	0.45	-	1.3	-	0.26	-
TA-11	0.9	0.1	0.3	0.25	1.28	-	0.17	-
TA-12	0.8	0.2	0.25	0.3	1.31	-	0.14	-
TA-16	0.9	0.1	0.2	1.08	0.6	-	0.12	-
TA-23	0.8	0.2	0.25	0.30	1.31	0.14	-	-
TA-34	0.84	0.15	0.25	0.18	1.28	0.25	-	0.06
TA-35	0.85	0.15	0.03	-	1.5	0.23	-	0.06
TA-56	0.87	0.13	0.17	0.18	1.29	0.24	-	0.06
TA-56D	0.87	0.13	0.16	0.17	1.23	0.23	-	0.06

TABLE 2

Alloy #	Max % H ₂ Conc. (H/(H+M))	Rev. % H ₂ Conc. (H/(H+M))	Plateau Pressure (Torr)
TA-1	1.84	1.6	2400
TA-2	>1.57	1.6	1130
TA-4	>1.56	1.6	3030
TA-5	1.83	1.5	660
TA-9	>1.55	1.6	1180
TA-10	2.0	1.6	5590
TA-11	1.78	1.5	7000
TA-12	1.9	1.72	2500
TA-16	1.75	1.19	5000
TA-23	1.99	1.71	1300
TA-34	1.87	1.55	1600
TA-56	1.84	1.7	7200
TA-56D	1.9	1.68	5700

The present invention includes a metal hydride hydrogen storage means for storing hydrogen within a container or tank. In one embodiment of the present invention, the storage means comprises the afore described hydrogen storage alloy material physically bonded to a support means. Generally, the support means can take the form of any structure that can hold the storage alloy material. Examples of support means include, but are not limited to, mesh, grid, matte, foil, foam and plate. Each may exist as either a metal or non-metal.

The support means may be formed from a variety of materials with the appropriate thermodynamic characteristics that can provide the necessary heat transfer mechanism. These include both metals and non-metals. Preferable metals include those from the group consisting of Ni, Al, Cu, Fe and mixtures or alloys thereof. Examples of support means that can be formed from metals include wire mesh, expanded metal and foamed metal.

The hydrogen storage alloy material may be physically bonded to the support means by compaction and/or sintering processes. The alloy material is first converted into a fine powder. The powder is then compacted onto the support means. The compaction process causes the powder to adhere to and become an integral part of the support means. After compaction, the support means that has been impregnated with alloy powder is preheated and then sintered. The preheating process liberates excess moisture and discourages oxidation of the alloy powder. Sintering is carried out in a high temperature, substantially inert atmosphere containing hydrogen. The temperature is sufficiently high to promote particle-to-particle bonding of the alloy material as well as the bonding of the alloy material to the support means.

The support means/alloy material can be packaged within the container/tank in many different configurations. Figure 6 shows a configuration where the support means/alloy material is spirally wound into a coil. Figure 7 shows an alternate configuration where the support means/alloy material is assembled in the container as a plurality of stacked disks. Other configurations are also possible (e.g. stacked plates).

Compacting and sintering alloy material onto a support means increases the packing density of the alloy material, thereby improving the thermodynamic and kinetic characteristics of the hydrogen storage system. The close contact between the support means and the alloy material improves the efficiency of the heat transfer into and out of the hydrogen storage alloy material as hydrogen is absorbed and desorbed. In addition, the uniform distribution of the support means throughout the interior of the container provides for an even temperature and heat distribution throughout the bed of alloy material.

This results in a more uniform rates of hydrogen absorption and desorption throughout the entirety thereof, thus creating a more efficient energy storage system.

One problem when using just alloy powder (without a support means) in hydrogen storage beds is that of self-compaction due to particle size reduction. That is, during repeated hydriding and dehydriding cycles, the alloy materials expand and contract as they absorb and desorb hydrogen. Some alloy materials have been found to expand and contract by as much as 25% in volume as a result of hydrogen introduction into and release from the material lattice. As a result of the dimensional change in the alloy materials, they crack, undergo fracturing and break up into finer and finer particles. After repeated cycling, the fine particles self-compact causing inefficient hydrogen transfer as well as high stresses that are directed against the walls of the storage container.

However, the processes used to attach the alloy material onto the support means keeps the alloy particles firmly bonded to each other as well as to the support means during the absorption and desorption cycling. Furthermore, the tight packaging of the support means within the container serves as a mechanical support that keeps the alloy particles in place during the expansion, contraction and fracturing of the material.

While the invention has been described in connection with preferred embodiments and procedures, it is to be understood that it is not intended to limit the invention to the described embodiments and procedures. On the contrary it is intended to cover all alternatives, modifications and equivalence which may be included within the spirit and scope of the invention as defined by the claims appended hereinafter.